

# Extraction of Oleic Acid from Soybean Oil and Jojoba Oil—Phase Diagrams

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**ABSTRACT:** Formamide, *N*-methylformamide, *N*-dimethylformamide, dimethylsulfoxide, 1,2-butanediol, and 2-butane-1,4-diol were considered as potential extractants of fatty acids from soybean and jojoba oils. Ternary liquid-liquid phase diagrams at 298.15 K, distribution, and selectivity coefficients of oleic acid are reported. Of the investigated solvents, only *N*-methylformamide and 1,2-butanediol have desirable extraction characteristics.

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**KEY WORDS:** Jojoba oil, liquid-liquid equilibrium, neutralization, refining, soybean oil.

Crude vegetable oils contain variable amounts of nonglyceride impurities, such as free fatty acids, phosphatides, and pigments. Most of these impurities are detrimental to the quality of the final product and must be removed. A variety of procedures may be involved in the conversion of crude vegetable oils to edible products. The most important reactions are degumming, neutralization, and bleaching. The amount of free fatty acids is a measure of the quality of the unrefined, as well as the refined, oil. Removal of fatty acids from edible and industrial oils is usually performed by the treatment of warm oils with sodium hydroxide, followed by centrifugal separation. This procedure has a number of disadvantages, the most important being the loss of triglycerides during saponification of the fatty acids. Because an excess of alkali is usually added over the amount necessary to neutralize the free fatty acids present, the process generates considerable quantities of effluent (1). Liquid-liquid extraction and membrane separation techniques have been considered as alternatives to the classical caustic soda refining process (1–6). However, previously tested extractants (mostly alcohols) show rather low distribution and selectivity coefficients and high mutual miscibility with treated oil.

Jojoba is unique among plants in that the nuts contain about 50% by weight of a practically odorless, colorless oil, which is composed mainly of the straight-chain monoesters of the monounsaturated  $C_{20}$  and  $C_{22}$  alcohols and acids, with one double bond at each side of the ester bond. The almost complete absence of glycerine indicates that jojoba differs radically from all known seed oils. It is not a fat but a liquid wax.

In the present work, a number of new solvents were considered as potential extractants of fatty acids. These solvents include: *N*-methylformamide, formamide, dimethylsulfoxide, 1,2-butanediol, and 2-butene-1,4-diol. 1,2-Butanediol has already been investigated by Keurentjes *et al.* (6) in the solvent extraction with hollow fibers of fatty acids ( $C_6$ – $C_{22}$ ) from soybean oil, but the main efforts were directed to mass transfer problems rather than to distribution studies. In contrast, our investigation is devoted to determination of ternary liquid-liquid diagrams at 298.15 K, for five systems with soybean oil and two with jojoba oil. Jojoba oil has been used to determine the possible influence of the oil structure on the liquid-liquid equilibrium characteristics. In all partition experiments, oleic acid ( $C_{18}$ ) served as a representative of fatty acids.

## EXPERIMENTAL PROCEDURES

Dimethylsulfoxide and *cis*-2-butene-1,4-diol were purchased from Merck (Darmstadt, Germany); *N*-methylformamide, *N*-dimethyl formamide, and 1,2-butanediol from Fluka (Buchs, Switzerland); and formamide and oleic acid from Aldrich (Milwaukee, WI). All reagents were analytical grade and were used without further purification. Commercially-available soybean oil of edible quality and jojoba oil (Israel Jojoba Ltd., Hatzetim, Israel) were used in the partition experiments.

The binodal curves in the ternary systems were determined by the weighing method in the following manner: increasing amounts of oleic acid were mixed in a thermostatted bath at 298.15 K with prepared oil-solvent solutions of known composition. Turbidity of these solutions was determined with a Turner Designs Nephelometer Model 40–100. A sharp increase in turbidity indicated formation of a new liquid phase. The distribution curves (tie-lines) were determined in separate experiments by preparing synthetic mixtures that fell within the two-phase region and separating the phases after equilibrium was attained. Each phase was then titrated for oleic acid with standard sodium hydroxide solutions. The tie-lines were located by simultaneously using the oleic concentration and the co-existence (binodal) curves. The results reported are the averages of three determinations. The overall error is considered to be less than 1% in the determination of the binodal curve and 3% in the determination of the tie-lines.

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## RESULTS AND DISCUSSION

$$w_1 + w_2 + w_3 = 1$$

[4]

The experimental results for the liquid–liquid phase equilibrium at 298.15 K for the ternary systems oleic acid (1) + oil (2) + solvent (3) are presented in Tables 1–6 and in Figures 1 and 2, where (1), (2), (3) represent the ID of the component. The data include experimental solubilities (coexistence curves), tie-lines, distribution coefficient  $D$ , and selectivity coefficient  $S$ , defined as

$$D = \frac{[w_1]_{\text{solvent}}}{[w_1]_{\text{oil}}} \quad [1]$$

$$S = \frac{\frac{[w_1]}{w_2}_{\text{solvent}}}{\frac{[w_1]}{w_2}_{\text{oil}}} \quad [2]$$

where  $w$  represents weight percent.

The coexistence curves can be accurately represented by the extended Setchenow Equation (Ref. 7):

$$w_3 = a_0 + a_1 w_1 + a_2 w_2 + a_{12} w_1 w_2 \quad [3]$$

where  $w_i$  are the weight mass fractions of components,  $a_i$  adjustable coefficients and

The coefficients of Equation 3 were evaluated by an unweighted multivariate least-squares method and are reported in Table 7, together with the pertinent coefficient of determination. The equilibrium partition of components between the oil and solvent phases was determined by a simultaneous solution of Equations 3 and 4 and from the known distribution of oleic acid (i.e., values  $[w_1]_{\text{oil}}$  and  $[w_1]_{\text{solvent}}$  from titration determinations).

Figures 1 and 2 can be used to analyze the effect of the nature of the oil (soybean and jojoba) and of the solvent (formamide and methylformamide) in the distribution of oleic acid: (i) Both figures show that the effect of oil structure on mutual solubility is not large: with formamide, jojoba oil is more soluble than soybean oil; with methylformamide the opposite is true. (ii) Partial blocking of the amido group of formamide with a methyl group (methyl formamide) produces a substantial increase in mutual solubility. Our experimental results indicate that blocking the amido group with an additional methyl group (dimethylformamide) results in complete miscibility—the three components can mix in any ratio without producing phase separation. (iii) Although solubility in formamide is smaller than in methylformamide, separation is poorer; the tie-lines essentially go through the solvent apex; two phases with substantially different composition are pro-

**TABLE 1**  
Coexistence (binodal) Curve in the Oleic Acid (1) + Soybean Oil (2) + 1,2-Butanediol (3) System at 298.15 K<sup>a</sup>

$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$
0.0000	0.9879	0.0121	0.2436	0.3190	0.4372
0.0318	0.9474	0.0208	0.2633	0.2999	0.4368
0.0584	0.8892	0.0523	0.2559	0.2343	0.5098
0.1159	0.8132	0.0708	0.2485	0.1135	0.6381
0.1560	0.7449	0.0991	0.2280	0.0908	0.6812
0.1768	0.6913	0.1319	0.1976	0.0537	0.7488
0.2170	0.5764	0.2067	0.1830	0.0406	0.7764
0.2297	0.4841	0.2862	0.1649	0.0327	0.8024
0.2395	0.5416	0.2190	0.1085	0.0165	0.8750
0.2551	0.4023	0.3426	0.0000	0.0075	0.9925

<sup>a</sup> $w$  = Weight percent; the numbers (1), (2), and (3) represent the ID of the component.

**TABLE 2**  
Equilibrium Partition of Components in the Oleic Acid (1) + Soybean Oil (2) + 1,2-Butanediol (3) System (tie-lines) and Distribution and Selectivity Coefficients of Oleic Acid<sup>a</sup>

Oil phase			Solvent phase			$D$	$S$
$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$		
0.0451	0.9234	0.0315	0.0439	0.0115	0.9449	0.97	77.4
0.0519	0.9141	0.0340	0.0490	0.0121	0.9389	0.94	71.3
0.1144	0.8183	0.0677	0.0912	0.0181	0.8907	0.80	36.0
0.1224	0.8041	0.0735	0.0973	0.0192	0.8835	0.79	33.3
0.1574	0.7350	0.1076	0.1303	0.0268	0.8429	0.83	22.7
0.1980	0.6326	0.1694	0.1888	0.0516	0.7596	0.95	11.7
0.2306	0.5186	0.2508	0.2589	0.1745	0.5666	1.12	3.3

<sup>a</sup> $w$  = Weight percent;  $D$  = distribution coefficient;  $S$  = selectivity distribution. See Table 1 for (1), (2), (3) explanation.

**TABLE 3**  
**Coexistence (binodal) Curve in the Oleic Acid (1) + Soybean Oil (2) + Dimethylsulfoxide (3) System at 298.15 K<sup>a</sup>**

$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$
0.0000	0.9518	0.0482	0.2126	0.1615	0.6259
0.1033	0.7990	0.0977	0.2129	0.1306	0.6567
0.1383	0.7545	0.1072	0.2068	0.1256	0.6676
0.2292	0.6147	0.1561	0.2224	0.1251	0.6524
0.2487	0.5365	0.2148	0.1929	0.1091	0.6980
0.2354	0.5339	0.2307	0.1764	0.0676	0.7561
0.2561	0.4524	0.2916	0.1053	0.0563	0.8384
0.2666	0.4030	0.3304	0.0466	0.0467	0.9067
0.2500	0.2501	0.4999	0.0000	0.0766	0.9234

<sup>a</sup>Abbreviation as in Table 1. See Table 1 for (1), (2), (3) explanation.**TABLE 4**  
**Equilibrium Partition of Components in the Oleic Acid (1) + Soybean Oil (2) + Dimethylsulfoxide (3) System (tie-lines) and Distribution and Selectivity Coefficients of Oleic Acid<sup>a</sup>**

Oil phase			Solvent phase			$D$	$S$
$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$		
0.0600	0.8922	0.0478	0.0184	0.0301	0.9515	0.31	8.8
0.0764	0.8669	0.0567	0.0242	0.0313	0.9445	0.32	8.8
0.1307	0.7776	0.0917	0.0477	0.0369	0.9154	0.36	7.7
0.1564	0.7316	0.1120	0.0615	0.0406	0.8979	0.39	7.1
0.1659	0.7137	0.1204	0.0672	0.0422	0.8906	0.41	6.9
0.1923	0.6612	0.1465	0.0845	0.0477	0.8678	0.44	6.1
0.2251	0.5868	0.1881	0.1098	0.0570	0.8332	0.49	5.0
0.2289	0.5773	0.1938	0.1130	0.0583	0.8287	0.49	4.9
0.2735	0.4294	0.2971	0.1561	0.0795	0.7644	0.57	3.1

<sup>a</sup>Abbreviations as in Table 2. See Table 1 for (1), (2), (3) explanation.**TABLE 5**  
**Coexistence (binodal) Curve in the Oleic Acid (1) + Soybean Oil (2) + *cis*-2-Butene -1,4-Diol (3) System at 298.15 K<sup>a</sup>**

$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$
0.0000	0.9008	0.0992	0.6604	0.0644	0.2751
0.0471	0.8665	0.0864	0.8644	0.0617	0.0739
0.0991	0.8249	0.0760	0.6089	0.0524	0.3387
0.1077	0.7795	0.1128	0.5642	0.0470	0.3888
0.1676	0.7649	0.0675	0.7659	0.0464	0.1876
0.2081	0.7381	0.0538	0.7822	0.0408	0.1770
0.2635	0.6957	0.0408	0.8447	0.0404	0.1149
0.2862	0.6601	0.0537	0.5962	0.0390	0.3647
0.3088	0.6257	0.0655	0.7488	0.0381	0.2131
0.3658	0.5920	0.0422	0.5969	0.0380	0.3650
0.4087	0.5480	0.0432	0.4943	0.0221	0.4836
0.4410	0.5296	0.0264	0.2103	0.0217	0.7680
0.4566	0.5003	0.0432	0.3564	0.0185	0.6250
0.4965	0.4639	0.0396	0.5129	0.0169	0.4701
0.5283	0.4459	0.0257	0.4706	0.0169	0.5125
0.5624	0.4248	0.0129	0.0528	0.0139	0.9333
0.5590	0.4146	0.0264	0.5435	0.0135	0.4430
0.5525	0.4081	0.0394	0.4041	0.0129	0.5830
0.5624	0.3931	0.0446	0.5295	0.0120	0.4585
0.5993	0.3871	0.0136	0.1018	0.0116	0.8865
0.6004	0.3698	0.0298	0.2501	0.0115	0.7384
0.6947	0.2851	0.0202	0.2426	0.0102	0.7471
0.7452	0.2345	0.0202	0.4650	0.0099	0.5251
0.7508	0.2110	0.0382	0.1472	0.0088	0.8440
0.8203	0.1608	0.0189	0.1983	0.0048	0.7969
0.8384	0.1136	0.0480	0.0000	0.0572	0.9428

<sup>a</sup>Abbreviation as in Table 1. See Table 1 for (1), (2), (3) explanation.

**TABLE 6**  
**Equilibrium Partition of Components in the Oleic Acid (1) + Soybean Oil (2) + *cis*-2-Butene-1,4-Diol (3) System (tie-lines) and Distribution and Selectivity Coefficients of Oleic Acid<sup>a</sup>**

Oil phase			Solvent phase			<i>D</i>	<i>S</i>
<i>w</i> <sub>1</sub>	<i>w</i> <sub>2</sub>	<i>w</i> <sub>3</sub>	<i>w</i> <sub>1</sub>	<i>w</i> <sub>2</sub>	<i>w</i> <sub>3</sub>		
0.0568	0.8539	0.0893	0.0035	0.0292	0.9673	0.062	1.80
0.1409	0.7813	0.0778	0.0078	0.0282	0.9640	0.055	1.53
0.1925	0.7374	0.0701	0.0097	0.0278	0.9625	0.050	1.34
0.2400	0.6971	0.0629	0.0109	0.0276	0.9615	0.045	1.15
0.2873	0.6570	0.0557	0.0118	0.0274	0.9608	0.041	0.99
0.3854	0.5726	0.0420	0.0123	0.0273	0.9604	0.032	0.67
0.4039	0.5564	0.0397	0.0123	0.0273	0.9604	0.039	0.62
0.4183	0.5422	0.0395	0.0226	0.0682	0.9092	0.050	0.43
0.5102	0.4607	0.0291	0.0126	0.0272	0.9602	0.025	0.42
0.5642	0.4098	0.0260	0.0134	0.0270	0.9596	0.024	0.36
0.6122	0.3629	0.0249	0.0151	0.0267	0.9582	0.025	0.34
0.6335	0.3416	0.0249	0.0163	0.0264	0.9573	0.026	0.33
0.6907	0.2824	0.0269	0.0208	0.0255	0.9537	0.030	0.33
0.7207	0.2503	0.0290	0.0242	0.0248	0.9510	0.034	0.34
0.7505	0.2174	0.0321	0.0242	0.0248	0.9510	0.032	0.28
0.8506	0.1001	0.0493	0.0509	0.0200	0.9291	0.060	0.30

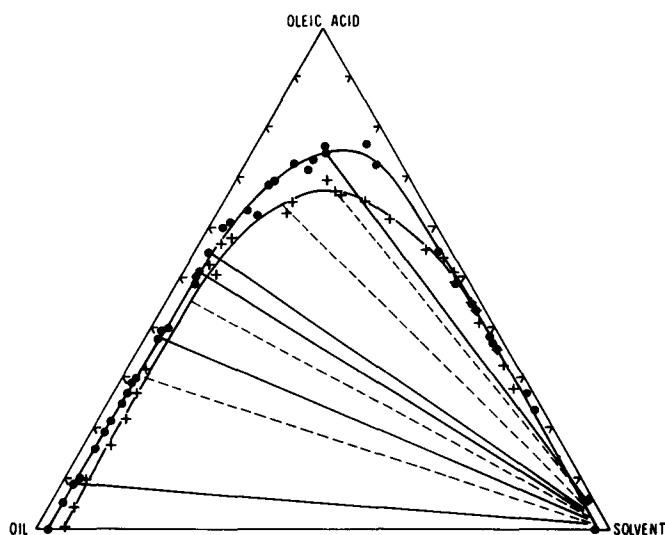
<sup>a</sup>Abbreviations as in Table 2. See Table 1 for (1), (2), (3) explanation.

duced, but on a solvent-free basis, they have the same composition. (iv) Partial blocking of the amido group substantially increases not only solubility but also the distribution coefficient, with *D* increasing at least by one order of magnitude. (v) According to Keurentjes *et al.* (6), soybean oil is essentially insoluble in 1,2-butanediol: our results (Tables 1 and 2) indicate that this is not true.

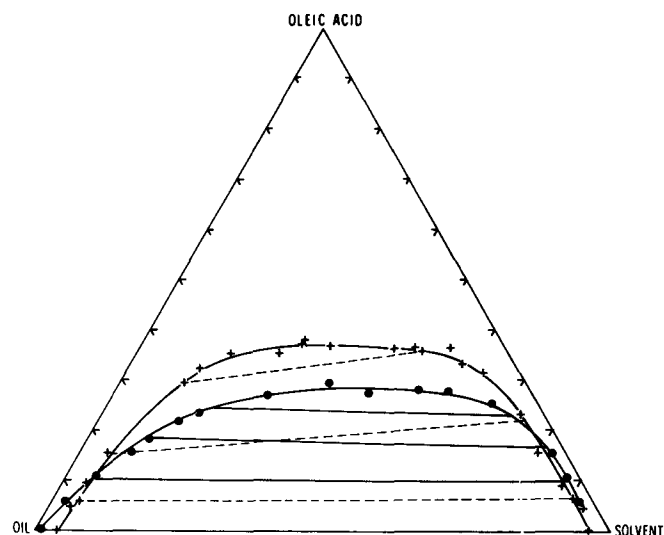
The distribution curves and the corresponding distribution coefficients *D* of oleic acid in the different oil-solvent systems appear in Figures 3 and 4. They show that, with the exception of *N*-methylformamide, the partition of oleic acid between the oil and the solvent is characterized by rather low distribution coefficients. For practical purposes, the lower the distribution coefficient, the larger the volume of extractant that will be needed for a given percentage removal of fatty

acids. On the other hand, however, the selectivity coefficients *S* of oleic acid in both soybean and jojoba oil have the highest values (Figs. 5 and 6) in the region of low fatty acid content, which is the region of industrial importance. The selectivity coefficients decrease rapidly as oleic acid concentration in the oil phase increases. Taking into account the values of distribution and selectivity coefficients, it seems that, of the tested solvents, only *N*-methylformamide and 1,2-butanediol meet the necessary requirements (distribution constant larger than one and high selectivity) to serve as extractants of fatty acids.

Knowledge of the phase diagram and the pertinent tie-lines allows calculation of the number of theoretical stages necessary for the desired reduction in the concentration of the fatty acid (8).



**FIG. 1.** Phase equilibrium diagram for the systems oleic acid + soybean oil + formamide (● —) and oleic acid + jojoba oil + formamide (+ - - - -). Not all tie-lines are shown.



**FIG. 2.** Phase equilibrium diagram for the systems oleic acid + soybean oil + *N*-methylformamide (● —) and oleic acid + jojoba oil + *N*-methylformamide (+ - - - -). Not all tie-lines are shown.

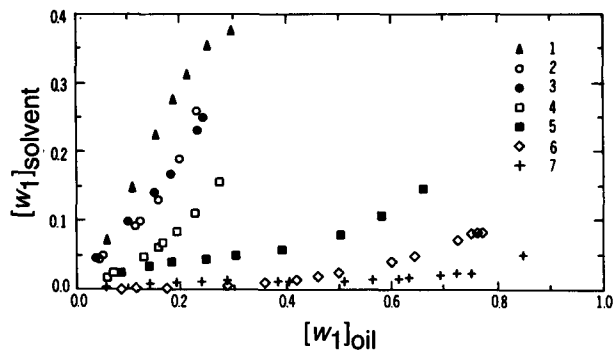
**TABLE 7**  
Coefficients of the Setchenow Equation (Ref. 1)

Solvent	$a_0$	$a_1$	$\frac{a_2}{a_3}$	$\frac{a_{12}}{a_{13}}$	$R^2$
1,2-Butanediol <sup>a</sup>	0.0238	-0.8600	4.0670	7.5341	0.9913
<i>N</i> -methylformamide <sup>a</sup>	0.1009	-1.3357	-4.6218	8.9864	0.9958
Formamide <sup>a</sup>	0.2341	-1.8506	-4.1280	-3.7622	0.9818
2-Butene-1,4-diol <sup>a</sup>	0.4838	-2.5731	-2.3080	-7.5341	0.9405
Dimethylsulfoxide <sup>a,c</sup>	0.0544	0.0898	-3.7877	2.4743	0.9262
<i>N</i> -methylformamide <sup>b</sup>	0.0727	-0.9700	-3.7845	2.0611	0.9889
Formamide <sup>b</sup>	0.1205	-1.4714	-3.3354	-4.0403	0.9915

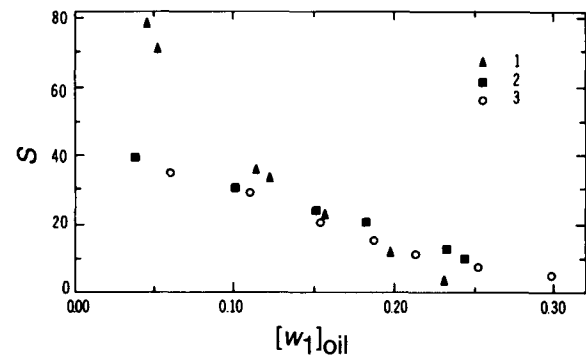
<sup>a</sup>Soybean oil.

<sup>b</sup>Jojoba oil.

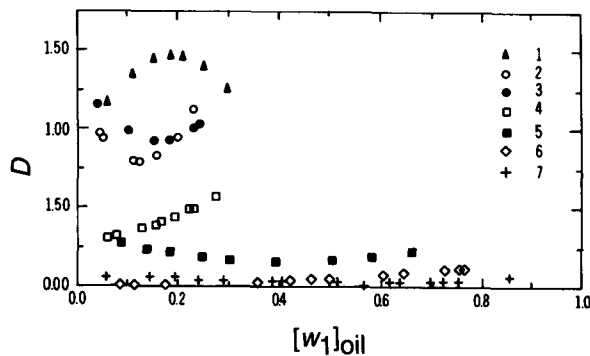
<sup>c</sup>The binodal curve for dimethylsulfoxide was:  $\ln w_2 = a_0 + a_1 w_1 + a_3 w_3 + a_{13} w_1 w_3$ .



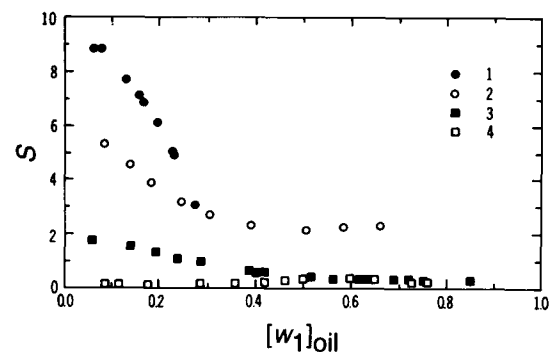
**FIG. 3.** Partition of oleic acid between the solvent and oil phases: 1, *N*-methylformamide + jojoba oil (JO); 2, 1,2-butanediol + soybean oil (SB); 3, *N*-methylformamide + SB; 4, dimethylsulfoxide + SB; 5, formamide + JO; 6, formamide + SB; 7, 2-butene-1,4-diol + SB. *W*, weight percent.



**FIG. 5.** Selectivity coefficient of oleic acid: 1, 1,2-butanediol + SB; 2, *N*-methylformamide + SB; 3, *N*-methylformamide + JO. Abbreviations as in Figure 3.



**FIG. 4.** Distribution coefficient of oleic acid. Key and abbreviation as in Figure 3.



**FIG. 6.** Selectivity coefficient of oleic acid: 1, dimethylsulfoxide + SB; 2, formamide + JO; 3, 2-butene-1,4-diol + SB; 4, formamide + SB. Abbreviations as in Figure 3.

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